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### (54) ELECTROPHOTOGRAPHIC TONER, BINARY DEVELOPER, AND IMAGE FORMING METHOD

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide the electrophotographic toner superior in powder characteristics, such as storage stability and good in offset resistance.

SOLUTION: This electrophotographic toner contains at least a binder resin and a colorant and a wax, and this wax has a heat absorption starting temperature of 40-120°C measured by a differential scanning calorimeter and a melting point of 80-120°C and a melt velocity of 1-200 centipoise at 120°C, and the toner particles have a form coefficient SF-1 (represented by formula I:  $SF-1 = R^2/S \times \pi/4 \times 100$ ) of 130-160, and that SF-2 (represented by formula II:  $SF-2 = T^2/S \times \pi/4 \times 100$ ) of 110-140, where R is a maximum diameter of the toner particles and S is a projection area of the toner particle and T is a peripheral length, and the toner particles have a specific surface area of 1.9-4.0 and a volume average particle diameter of 3-10  $\mu\text{m}$ .

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CLAIMS

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[Claim(s)]

[Claim 1] In the toner for electrophotography which contains binding resin, a coloring agent, and a wax at least The endoergic initiation temperature measured with the differential scanning calorimeter of said wax is 40-120 degrees C. Melting temperature is 80-120 degrees C, and the melt viscosity in 120 degrees C is one to 200 centipoise. And shape factor SF-1 expressed with the following type (1) of this toner for electrophotography is 130-160. The toner for electrophotography characterized by for shape factor SF-2 expressed with the following type (2) being 110-140, for specific surface area being 1.9-4.0, and volume mean particle diameter being 3-10 micrometers.

[Equation 1]

$$(1) \quad SF-1 = \frac{R^2}{S} \times \frac{\pi}{4} \times 100$$

$$(2) \quad SF-2 = \frac{T^2}{S} \times \frac{1}{4\pi} \times 100$$

(However, R expresses the maximum length of toner particle diameter, S expresses the projected area of a toner particle, and T expresses the boundary length of the projection image of a toner particle.)

[Claim 2] The binary system developer characterized by including the toner for electrophotography and a carrier according to claim 1.

[Claim 3] The development process which develops with a toner the electrostatic latent image formed on latent-image support, and forms a toner image, In the image formation approach including the imprint process which imprints this toner image on imprint material, and forms a transfer picture, and the fixation process established in this transfer picture The image formation approach which said toner is a toner for electrophotography according to claim 1, and is characterized by being established without said fixation process minding the oil for mold release substantially.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the image formation approach using the toner for electrophotography and it which are used for a xerography, an electrostatic recording method, an electrostatic printing method, etc.

[0002]

[Description of the Prior Art] the case where an image can be conventionally formed in a copying machine, a laser beam printer, etc. -- general -- Carlsson -- law is used. The electrostatic latent image by which the conventional image formation approach was formed on the photo conductor with the optical means is imprinted by record media, such as the recording paper, at an imprint process, after negatives are developed at a development process, it is a fixation process next and, generally record media, such as the recording paper, are fixed to it by heat and the pressure. And cleaning equipment is installed in order to remove the residual toner which remains on a photo conductor after an imprint since the above-mentioned photo conductor is used repeatedly.

[0003] Although the development method used for the development of this electrostatic latent image has the 2 component developing-negatives method using the 1 component developing-negatives method, toner, and carrier which use only a toner Since the considerable extent control of the amount of frictional electrifications of a toner can be carried out by selecting the property of a carrier, and churning conditions since frictional electrification of the toner is carried out by agitating a toner and a carrier, the dependability of image quality is highly excellent in the two component developer of the 2 component developing-negatives method.

[0004] Moreover, although there is a heating fixation method by the heating roller or the heating film as a method established in a toner image, the heating mechanical control by roller is widely used from thermal efficiency being good and high-speed fixation being possible. However, a heating fixation method makes the so-called offset phenomenon with which some toner images adhere to a heating roller, and the adhering toner is re-imprinted and pollutes a copy image generate in order to contact under application of pressure of the front face of a heating roller and the toner image of a melting condition. For the purpose of preventing this phenomenon, the front face of a heating roller is formed with silicone rubber and a fluoro resin excellent in the mold-release characteristic over a toner, and the approach of supplying mold-release characteristic liquids, such as silicone oil, to that front face further is taken. Equipment to supply said mold-release characteristic liquid in that the offset phenomenon of a toner is prevented, although this approach is very effective is needed. Said mold-release characteristic liquid is heated and this not only serves as hindrance of the miniaturization of equipment, and lightweight-izing, but evaporates, and an unpleasant smell may be given or it may produce contamination inside the plane.

[0005] the approach (a JP,1-133065,A official report --) of limiting the viscosity of a toner, in order to solve a problem with said such mold-release characteristic liquid A JP,2-161466,A official report, a JP,2-100059,A official report, JP,3-229265,A, How (Japanese Patent Publication No. No. 3304 [ 52 to ]

official report) to make waxes, such as resin which has a mold-release characteristic in a toner, contain, the approach (a JP,3-260659,A official report --) of limiting the melt viscosity of a wax JP,3-122660,A, the approach (JP,7-84398,A official report) of limiting the path of a wax domain and the abundance on the front face of a toner of a wax, the approach (JP,6-161145,A official report) of limiting a wax domain configuration, etc. are proposed.

[0006] Moreover, about the heating fixation method by the heating film, various proposals are made from a viewpoint of fixable [ more stable ] and energy saving. For example, the binding resin which is the constituent of a toner, and the approach (JP,3-122661,A) of limiting the viscosity of a release agent are proposed for the purpose of controlling an offset phenomenon more. Thus, various proposals to fixable are made. However, the actual condition is that what fully satisfied coexistence with the fine-particles property (especially shelf life) of a toner and the fixation property of not using the oil for mold release substantially is not yet obtained.

[0007]

[Problem(s) to be Solved by the Invention] This invention solves the problem in said former, and makes it a technical problem to attain the following objects. Namely, this invention aims at excelling in fine-particles properties, such as preservation stability, and offering the good toner for electrophotography of offset-proof nature, a binary system developer, and the image formation approach using it.

[0008]

[Means for Solving the Problem] Said The means for solving a technical problem is as follows.

<1> In the toner for electrophotography which contains binding resin, a coloring agent, and a wax at least The endoergic initiation temperature measured with the differential scanning calorimeter of said wax is 40-120 degrees C. Melting temperature is 80-120 degrees C, and the melt viscosity in 120 degrees C is one to 200 centipoise. And shape factor SF-1 expressed with the following type (1) of this toner for electrophotography is 130-160. It is the toner for electrophotography characterized by for shape factor SF-2 expressed with the following type (2) being 110-140, for specific surface area being 1.9-4.0, and volume mean particle diameter being 3-10 micrometers.

[0009]

[Equation 2]

$$(1) \quad SF-1 = \frac{R^2}{S} \times \frac{\pi}{4} \times 100$$

$$(2) \quad SF-2 = \frac{T^2}{S} \times \frac{1}{4\pi} \times 100$$

[0010] (However, R expresses the maximum length of toner particle diameter, S expresses the projected area of a toner particle, and T expresses the boundary length of the projection image of a toner particle.)

<2> It is the binary system developer characterized by including the toner for electrophotography and carrier of a publication in the above <1>.

<3> The development process which develops with a toner the electrostatic latent image formed on latent-image support, and forms a toner image, In the image formation approach including the imprint process which imprints this toner image on imprint material, and forms a transfer picture, and the fixation process established in this transfer picture Said toner is a toner for electrophotography given in the above <1>, and it is the image formation approach characterized by being established without said fixation process minding the oil for mold release substantially.

[0011] Furthermore, said The means for solving a technical problem has the following desirable modes.

<4> The toner for electrophotography given in the above <1> containing the copolymerization resin of a styrene system monomer and an indene system monomer is desirable.

<5> The mole ratios of said styrene system monomer and said indene system monomer are 40:60-80:20, and the toner for electrophotography given in the above <4> whose softening temperature Tm of said copolymerization resin is 100-170 degrees C is desirable.

<6> The toner for electrophotography given in the above <1> containing with an aliphatic hydrocarbon-

carbon numbers of nine or more aromatic hydrocarbon copolymerization petroleum resin, <4> or, and <5> is desirable.

<7> The toner for electrophotography given in the above <6> whose weight ratios of the aromatic hydrocarbon monomer and aliphatic hydrocarbon monomer of with an aliphatic hydrocarbon-carbon numbers [ said ] of nine or more aromatic hydrocarbon copolymerization petroleum resin are 99:1-50:50 is desirable.

<8> The above <1> said whose binding resin is polyester resin, and the toner for electrophotography given in either of <4> to <7> are desirable.

<9> The development process which develops with a toner the electrostatic latent image formed on latent-image support, and forms a toner image, In the image formation approach including the imprint process which imprints this toner image on imprint material, and forms a transfer picture, and the fixation process established in this transfer picture The image formation approach which said toner is a toner for electrophotography given in either of <8> from the above <4>, and is characterized by being established without said fixation process minding the oil for mold release substantially is desirable.

[0012] According to the toner for electrophotography of this invention, when treated within a copying machine as fine particles, even if there is no problem in the fluidity and whenever [ copying machine internal temperature ] goes up from 40 degrees C to about 50 degrees C, a toner does not condense. Since endoergic initiation temperature is 40-120 degrees C with the DSC curve by which the wax used for this invention is measured with a differential scanning calorimeter, the wax exposure part on the front face of a toner cannot fuse this easily, it is, and things are mentioned. Therefore, even if an external additive is buried in a toner for stress, such as stirring, it is hard coming to condense a toner. On the other hand, when imprinted material is fixed to a toner with heat and/or a pressure, a wax is fully eluted out of a toner, a wax layer is formed in the maximum upper layer of a toner layer, and the outstanding offset-proof nature is demonstrated.

[0013] This is considered as follows. The wax added in a toner forms a domain [ at least ] smaller than toner particle size, and is distributing it in a toner. A function is demonstrated in a wax being eluted from a toner and existing in the interface of a fixation roll and a toner at the time of fixation. However, it cannot be eluted, but only the wax which exists in a toner front face or exists very near table Men clearly is eluted, and all the waxes distributed in a toner can be contributed to fixation. Ideally, it is good to make distribution of a wax unevenly distributed near the toner front face.

[0014] Even if it does not raise the exposure surface ratio of the wax occupied on a toner front face by making a toner configuration into an infinite form comparatively in this invention, a large exposure area of a wax can be taken as a whole. Thereby, a wax is fully eluted out of a toner. Moreover, since the melt viscosity of a wax is low enough, it is thought that it can flow out of a toner promptly.

[0015]

[Embodiment of the Invention] Hereafter, the toner for electrophotography of this invention is explained to a detail.

[The toner for electrophotography]

(Shape factor of a toner) Shape factor SF-2 to which shape factor SF-1 to which the toner for electrophotography of this invention is expressed with the following type (1) is 130-160, and it is expressed with the following type (2) are 110-140.

[0016]

[Equation 3]

$$(1) \quad SF-1 = \frac{R^2}{S} \times \frac{\pi}{4} \times 100$$

$$(2) \quad SF-2 = \frac{T^2}{S} \times \frac{1}{4\pi} \times 100$$

[0017] However, R expresses the maximum length of toner particle diameter, S expresses the projected area of a toner particle, and T expresses the boundary length of the projection image of a toner particle.

[0018] The shape factor of a toner is used as a multiplier expressing gestalten, such as a configuration of a toner, and can be measured with an image analyzer (roux ZEKKUSU 5000, Japanese regulator company make) based on a statistical method which can carry out quantitative analysis of the area of the image which the optical microscope etc. caught, die length, the configuration, etc. to high degree of accuracy and which is called image analysis.

[0019]  $\pi/4$  is hung on the value which broke by projected area of a toner particle the value which carried out the square of the maximum length of the path of a toner particle, and also shape factor SF-1 is a numeric value doubled and acquired 100, it becomes a value near 100, so that its configuration of a toner particle is close to a ball, and it becomes a bigger value than 100, so that the configuration of a toner particle is long and slender, so that clearly from said formula (1). That is, the difference of the overall diameter of a toner particle and the diameter of min, i.e., distortion, is expressed. It becomes a value near 100, so that  $1/4\pi$  is hung on the value which broke by projected area of a toner particle the value to which shape factor SF-2 carried out the square of the boundary length of the projection image of a toner particle so that clearly from said formula (2) on the other hand, and also it is the numeric value doubled and acquired 100 and the configuration of a toner particle is close to a ball, and it becomes a value with what [ bigger ] has a surrounding more complicated configuration than 100. That is, toner surface area (irregularity nature) is expressed. If it is a perfect globular form, it is  $SF-1=Sf-2=100$ .

[0020] Although fixable becomes better as the exposure area on the front face of a toner of a wax is large, it is that a toner becomes an infinite form and this is attained. Conversely, if shape factor SF-1 is so smaller that [ that is, ] it is close to a globular form than 130, and if shape factor SF-2 are smaller than 110, the exposure area on the front face of a toner of a wax will be small, and the width of face of the fixation temperature which can be established without being accompanied by generating of offset will become narrow. however -- although it is satisfactory to fixable if shape factor SF-1 is larger than 160, for example when it is not much alike and becomes an infinite form too much, and when shape factor SF-2 are larger than 140 -- the developer layer nonuniformity on a development sleeve -- generating -- image nonuniformity -- becoming -- low -- it will become a dignified image. As for shape factor SF-1, 140-160 are desirable. Moreover, as for shape factor SF-2, 120-140 are desirable.

[0021] The volume mean particle diameter of the toner for electrophotography of this invention is 3-10 micrometers, and its 3-8 micrometers are desirable. In order to produce a clearer image, the smaller one of the volume mean particle diameter of this toner is good. If the volume mean particle diameter of this toner is larger than 10 micrometers, a high-definition image will no longer be obtained. On the other hand, if the volume mean particle diameter of this toner is smaller than 3 micrometers, electrostatic adhesion force will become large compared with gravity, and handling as fine particles will become difficult.

[0022] (Specific surface area) Specific surface area is 1.9-4.0, and the toners for electrophotography of this invention are 1.9-3.0 preferably. The specific surface area in this invention means BET surface area. Even if it does not raise the exposure surface ratio of the wax occupied on a toner front face by enlarging toner surface area, a large exposure area of a wax can be taken as a whole. Thereby, a wax is fully eluted out of a toner. Moreover, since the melt viscosity of a wax is low enough, it is thought that it can flow out of a toner promptly.

[0023] If specific surface area (BET surface area) is smaller than 1.9, there will be few elution volumes of a wax and the width of face of the fixation temperature which can be established without being accompanied by generating of offset will become narrow. On the other hand, when specific surface area (BET surface area) is larger than 4.0, there is much irregularity with a small toner front face, and very many non-subtlety powder added on a toner front face is needed. Although this non-subtlety powder is indispensable to the improvement of the shelf life of a toner, conveyance nature, development nature, and imprint nature, if many [ too ], the electrification maintenance nature as a developer and the color enhancement of a fixation image will fall. BET surface area can be measured with specific surface area and a pore distribution measuring device (coal tar SA3100 mold, coal tar company make).

[0024] At least, the toner for electrophotography of this invention contains binding resin, a coloring agent, and a wax, and comes to contain other components if needed further.

[0025] (Wax) With the DSC curve measured with a differential scanning calorimeter, endoergic initiation temperature is 40-120 degrees C, and said wax is 45-100 degrees C preferably. If this endoergic initiation temperature is lower than 40 degrees C, condensation of a toner will occur within a copying machine and a toner bottle. On the other hand, if this endoergic initiation temperature is higher than 120 degrees C, it will fully be hard to fuse a wax at the time of fixation, and will become easy to generate offset, and a non-offsetting field will become narrow. Said endoergic initiation temperature is influenced in the class of polar group which the thing of low molecular weight and its structure have among the molecular weight distributions which constitute a wax, and an amount. Although endoergic initiation temperature will also rise with the melting point if macromolecule quantification is generally carried out, in this way, the low melting temperature of wax original and hypoviscosity will be spoiled. Therefore, although it is effective to sort out and remove only the thing of these low molecular weight among the molecular weight distributions of a wax, there are approaches, such as molecular distillation, solvent separation, and gas-chromatograph judgment, as this approach.

[0026] The melting temperature is 80-120 degrees C, and said wax is 80-110 degrees C preferably. When the change temperature of a wax has past [ the low one ] and blocking resistance inferior in the melting temperature of said wax at less than 80 degrees C or the temperature in a copying machine increases, development nature gets worse. On the other hand, although the change temperature of a wax should just perform past [ the high one ] and fixation in an elevated temperature when this melting temperature exceeds 120 degrees C, it is not desirable in the viewpoint of energy saving.

[0027] The melt viscosity in 120 degrees C is one to 200 centipoise, and said wax is one to 100 centipoise preferably. If this melt viscosity is higher than 200 centipoises, the elution from a toner will be weak and fixation detachability will serve as imperfection.

[0028] The addition to the toner of said wax has 1 - 15 desirable % of the weight, and its 3 - 8 % of the weight is more desirable. If there are few these additions than 1 % of the weight, sufficient fixation latitude (temperature requirement of the fixation roll which can be established without being accompanied by offset of a toner) may not be obtained, and on the other hand, if there are more these additions than 10 % of the weight An isolation wax adheres to the front face of the photo conductor which the amount of waxes which \*\*\*\*s and is isolated from a toner increases, and the fine-particles fluidity of a toner gets worse, and forms an electrostatic latent image, and an electrostatic latent image may be unable to form in accuracy. Moreover, since transparency is inferior in a wax as compared with binding resin, the transparency of images, such as OHP, may fall and may serve as a dark projection image.

[0029] As a wax used for this invention, paraffin wax and its derivative, a montan wax and its derivative, a micro crystallin wax and its derivative, the Fischer Tropsch wax and its derivative, a polyolefine wax, its derivative, etc. are mentioned, for example. With a derivative, oxide, a polymer with a vinyl monomer, and a graft denaturation object are included. In addition, a vegetable system wax, an animal system wax, a mineral system wax, ester wax, etc. can be used. Moreover, alcohol, a fatty acid, an acid amide, etc. are mentioned as a wax for vinyl system polymers.

[0030] As said binding resin, for example Styrene, such as styrene and chloro styrene, (Binding resin) Monoolefins, such as ethylene, a propylene, a butylene, and an isoprene, Vinyl ester, such as vinyl acetate, propionic-acid vinyl, benzoic-acid vinyl, and vinyl acetate, A methyl acrylate, an ethyl acrylate, butyl acrylate, acrylic-acid dodecyl, Acrylic-acid octyl, acrylic-acid phenyl, a methyl methacrylate, ethyl methacrylate, alpha-methylene aliphatic series monocarboxylic acid ester, such as methacrylic-acid butyl and methacrylic-acid dodecyl, A homopolymer or copolymers, such as vinyl ether, such as vinyl methyl ether, vinyl ethyl ether, and vinyl butyl ether, a vinyl methyl ketone, a vinyl hexyl ketone, and a vinyl isopropenyl ketone, are mentioned. [ , such as a vinyl ketone ]

[0031] As typical binding resin, a polystyrene and styrene-acrylic-acid alkyl copolymer, a styrene-alkyl methacrylate copolymer, a styrene acrylonitrile copolymer, a styrene-butadiene copolymer, a styrene maleic anhydride copolymer, polyethylene, and polypropylene are mentioned especially. Furthermore, polyester, polyurethane, an epoxy resin, silicon resin, a polyamide, denaturation rosin, paraffin, and waxes are mentioned. Also in these, especially polyester is mentioned preferably. for example, the line



which consists of a polycondensation object which used bisphenol A and multiple-valued aromatic carboxylic acid as the main monomer component -- polyester resin is mentioned preferably.

[0032] The polyester resin used for this invention is compounded by the polycondensation from a polyol component and a polycarboxylic acid component. As said polyol component, ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 2, 3-butanediol, a diethylene glycol, triethylene glycol, 1, 5-butanediol, 1,6-hexanediol, neopentyl glycol, cyclohexane dimethanol, hydrogenation bisphenol A, bisphenol A and an ethyleneoxide addition product, bisphenol A, a propylene oxide addition product, etc. are mentioned.

[0033] As said polycarboxylic acid component, maleic-acid, fumaric-acid, phthalic-acid, isophthalic acid, terephthalic-acid, succinic-acid, dodecenyl succinic-acid, trimellitic acid, pyromellitic acid, cyclohexane tricarboxylic acid, 2 and 5, 7-naphthalene tricarboxylic acid, 1 and 2, 4-naphthalene tricarboxylic acid, 1 and 2, 5-hexane tricarboxylic acid, 1, and 3-dicarboxyl-2-methylene

KARUBOKISHIPUROPAN tetramethylen carboxylic acids and those anhydrides are mentioned.  
[0034] Moreover, the resin 5-30, and whose hydroxyl value 8000-150000, and the acid number are [ softening temperature / 90-150 degrees C and a glass transition point / 55-75 degrees C and number average molecular weight ] 5-40 for 3000-8000, and weight average molecular weight can use it preferably especially.

[0035] As said coloring agent, for example Carbon black, Nigrosine, (Coloring agent) The aniline blue, cull coil blue, chrome yellow, ultra marine blue, E. I. du Pont de Nemours oil red, quinoline yellow, methylene-blue chloride, A copper phthalocyanine blue, the Malachite Green OKISA rate, lamp black, A rose bengal, C. I. pigment red 48: 1, the C.I. pigment red 122, the C.I. pigment red 57:1, the C.I. pigment yellow 97, the C.I. pigment yellow 12, the C.I. pigment blue 15:1, and C.I. pigment blue 15:3 grade as a typical thing it is mentioned.

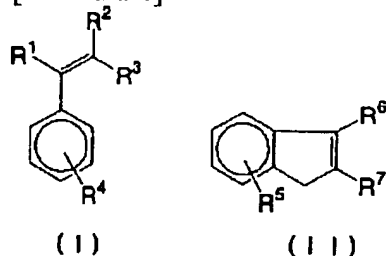
[0036] (Other components) As a component of said others, it is desirable that the copolymerization resin of a styrene system monomer and an indene system monomer and with an aliphatic hydrocarbon-carbon numbers of nine or more aromatic hydrocarbon copolymerization petroleum resin contain in a toner. By making a toner contain these resin, with the toner produced by kneading, grinding, and the classification, a toner becomes is easy to be ground and the shape factor of a toner can be enlarged.

[0037] When using polyester resin as <styrene-indene copolymerization resin> binding resin and a toner is made to contain the copolymerization resin of a styrene system monomer and an indene system monomer with binding resin, since the preservation stability of a toner constituent improves more, it is desirable. Said copolymerization resin has high softening temperature with low molecular weight (low melt viscosity), and the balance of further phase solubility with various resin, an elastomer, and a wax has the description of being good. While being able to raise the heat shelf life of a toner constituent by carrying out the melting blend of said copolymerization resin with binding resin, the grindability of a toner is desirable also at the point which can raise the productivity of a toner by becoming high. Furthermore, it is desirable also at the point of not affecting the electrification property of a toner greatly, either.

[0038] Especially, the copolymerization resin of the styrene system monomer expressed with the following general formula (I) and the indene system monomer expressed with the following general formula (II) is desirable.

[0039]

[Formula 1]



[0040] Among said general formula (I), R1, R2, R3, and R4 may be the same, or they may differ from each other, and express a hydrogen atom or a with a carbon number of four or less alkyl group. As a with a carbon number of four or less alkyl group, a methyl group, an ethyl group, a propyl group, butyl, etc. are mentioned, for example. As an example of a styrene system monomer expressed with said general formula (I), styrene, vinyltoluene, alpha methyl styrene, isopropyl toluene, etc. are mentioned. Especially, isopropyl toluene is desirable.

[0041] Among said general formula (II), R5, R6, and R7 may be the same, or they may differ from each other, and express a hydrogen atom or a with a carbon number of six or less alkyl group. As a with a carbon number of six or less alkyl group, a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical, a hexyl group, etc. are mentioned. An indene, a methyl indene, an ethyl indene, etc. are mentioned as an example of an indene system monomer expressed with said general formula (II). Especially, an indene is desirable.

[0042] As for the mole ratio of said styrene system monomer and said indene system monomer, it is desirable that it is 40:60-80:20. In addition, if a monomer with high purity is used, since it can control coloring and that an odor occurs in a production process at the time of heating, it is more desirable. The process of said copolymerization resin is indicated in detail by JP,6-184249,A.

[0043] As for said copolymerization resin, it is desirable to carry out 1-20 weight section content to the binding resin 100 weight section into a toner, and it is more desirable to carry out 3-15 weight section content. When it will become easy for the preservation stability of a toner to fall if this content is under 1 weight section, and 20 weight sections are exceeded, the transparency of a color picture may be reduced.

[0044] As for the ring and ball softening point of said copolymerization resin, it is desirable that it is 100-170 degrees C. When an image deficit may fall when this softening temperature is less than 100 degrees C, and it exceeds 170 degrees C, it may worsen low-temperature fixable one.

[0045] <Copolymerization petroleum resin> with with an aliphatic hydrocarbon-carbon numbers [ said ] of nine or more aromatic hydrocarbon copolymerization petroleum resin ("copolymerization petroleum resin" is only called hereafter.) The diolefin and monoolefin which are contained in the decomposition oil fraction which carries out a byproduction from the ethylene plant which manufactures ethylene, a propylene, etc. according to steam cracking of petroleum are compounded as a raw material. it is chosen out of an isoprene, piperylene, a 2-methyl-1-butene, and a 2-methyl-2-butene -- with one or more sorts of aliphatic hydrocarbon monomers at least The thing which is chosen from vinyltoluene, alpha methyl styrene, an indene, and isopropenyl toluene and to which copolymerization of one or more sorts of aromatic hydrocarbon monomers was carried out at least is desirable.

[0046] If a pure monomer with high monomer purity is used as said aromatic hydrocarbon monomer, since coloring of resin and the odor at the time of heating can be pressed down low, it is more desirable. As purity of said aromatic hydrocarbon monomer, 95% or more is desirable, and 98% or more is more desirable. As for said aromatic hydrocarbon monomer, it is desirable that a carbon number consists of nine or more monomers, and, in the case of the copolymerization petroleum resin obtained from this monomer and an aliphatic hydrocarbon monomer, the compatibility of binding resin, for example, polyester resin, becomes higher compared with the copolymerization petroleum resin with which a carbon number is obtained from less than nine aromatic hydrocarbon monomer and an aliphatic hydrocarbon monomer.

[0047] Furthermore, as a configuration of said copolymerization petroleum resin with which are satisfied of the grindability and heat shelf life of a toner, the direction with many amounts of aromatic hydrocarbon monomers is desirable. However, if there are too many aliphatic hydrocarbon monomers, since the dispersibility of a wax will worsen if there are too many aromatic hydrocarbon monomers, and heat shelf life etc. will fall on the other hand, as for the weight ratio of an aromatic hydrocarbon monomer and an aliphatic hydrocarbon monomer, 99:1-50:50 are desirable, 98:2-60:40 are more desirable, and 98:2-especially 90:10 are desirable.

[0048] In <additive> this invention, fixation assistants, such as a wax which raises fixable as an internal additive to a toner, and the electrification control agent which adjusts electrification can be added.

furthermore, independent [ in inorganic powder and resin powder ] on a toner front face, in order to raise more the mothball nature of a toner, a fluidity, development nature, and imprint nature -- or you may use together and add. As inorganic powder, infinite form powder, such as spherical particles, such as PMMA, nylon, a melamine, benzoguanamine, and a fluorine system, a vinylidene chloride, and a fatty-acid metal salt, is mentioned, for example as carbon black, a silica, an alumina, a titania, a zinc oxide, and resin powder. When adding inorganic powder or resin powder on a toner front face, each addition has 0.5 - 4 desirable % of the weight to a toner, and its 0.5 - 3 % of the weight is more desirable.

[0049] (The manufacture approach of a toner) In the toner for electrophotography of this invention, kneading processing is performed for adding said internal additive inside a toner particle. It can carry out using various kinds of heating kneading machines as kneading at this time. As this heating kneading machine, 3 forging roll dice, a 1 shaft screw mold, a 2 shaft screw mold, and a Banbury mixer mold are mentioned.

[0050] The manufacturing method of the toner for electrophotography of this invention controlled by the specific value has the arbitrary shape factor of a toner. In order to control a shape factor by the production process, selection of grinding methods, such as a collision plate type of a kneading object and a jet type, is mentioned. Although the thing which makes a toner collide with a certain object like a collision plate type is called surface grinding mold, there are a micronizer, Ur Max, and a Jet-o-mizer, for example. Moreover, although the thing which makes toners collide is called bulk crushing mold, there are KTM (krypton), a turbo mill, etc. Furthermore, the volume / surface grinding mold with which form a collision plate in a bulk crushing mold, and it has mold and both property have I type Jet-Mill.

[0051] Generally, in a bulk crushing mold, a grinding object tends to become an infinite form, and it is easy to become round in a surface grinding mold compared with it. Moreover, a configuration changes also with the counts of classification. It is easy to become round, so that there are many counts of classification. Furthermore, a configuration can be changed and conglobation by hot blast can also be raised by adding a hybridization system (made in the Nara machine factory), a mechano fusion system (Hosokawa Micron CORP. make), a KURIPU TRON system (Kawasaki Heavy Industries, Ltd. make), etc. as a process after that.

[0052] Although the toner for electrophotography of [binary system developer] this invention may be used by whichever of a 1 component development method and a 2 component development method, it is desirable to use by the 2 component development method combined with the resin coat carrier. By using a resin coat carrier as a carrier, the greasing and concentration nonuniformity which come from the standup of electrification by diameter[ of a granule ]-izing of a toner, aggravation of electrification distribution, and lowering of the amount of electrifications are improvable.

[0053] Especially if a carrier is a well-known carrier, it is not restricted, and an iron powder system carrier, a ferrite system carrier, a surface coat ferrite carrier, etc. can be used for it. Moreover, each surface addition powder may perform desired surface treatment, and may be used.

[0054] The toner for electrophotography of this invention of a configuration can be suitably used for the image formation approach including the development process which develops conventionally the well-known image formation approach, i.e., the electrostatic latent image formed on latent-image support, with a toner, and forms a toner image, the imprint process which imprints this toner image on imprint material, and forms a transfer picture, and the fixation process established in this transfer picture. Since the image formation approach of this invention using the toner for electrophotography of this invention is established without minding the oil for mold release substantially in a fixation process, it can avoid the problem accompanying the activity of the oil for mold release, and can offer the good image formation approach of offset-proof nature.

[0055] The front face of the fixation roll which is a fixation process and is used is the object to which a toner is not made to adhere, and it is desirable to form with the ingredient which was excellent in the mold-release characteristic to the toner, for example, silicone rubber, fluororesin, etc. Under the present circumstances, few [ infinite ] things of mold-release characteristic liquids, such as silicone oil applied to a fixation roll, are desirable. Although said mold-release characteristic liquid is effective, in order to transfer it to the imprinted material to which it is fixed to fixation latitude, there are problems -- that

there is greasiness and a tape cannot be stuck and an alphabetic character cannot be added in the Magic (trademark). This is remarkable about OHP. Moreover, since said mold-release characteristic liquid cannot make smooth the roughness on the front face of fixation, it causes lowering of the transparency of OHP.

[0056] Since sufficient fixation latitude is shown, even if the toner for electrophotography of this invention does not apply mold-release characteristic liquids, such as silicone oil, to a fixation roll at all or applies them to it, they are few on it and good for it. For example, it is good in below 1micro liter per one sheet of A4 form. If it is the range of this level, many above-mentioned problems are avoidable on parenchyma. Especially the anchorage device that is a fixation process and is used is not restricted, and a well-known roll-roll contact mold anchorage device, a roll-belt contact mold anchorage device, etc. can be conventionally used for it.

[0057]

[Example] Hereafter, although the example of this invention is explained, this invention is not limited at all by these examples. In addition, all the "sections" in an example means the "weight section."

[0058]

(Example 1)

a line -- polyester ..... The 87 sections (4,000 the line obtained from a terephthalic acid / bisphenol A and an ethylene oxide addition product / cyclohexane dimethanol polyester: Tg= 62 degrees C, Mn= Mw= 35,000 acid number = 12 and water acid-number = 25)

a Magenta pigment (C. I. pigment red 57) ..... 3 section wax A ..... The five sections (120 degree-C [ behenic acid stearyl, endoergic initiation temperature: 47 degree C, and ] o'clock of melt viscosity: 50 centipoises)

Copolymerization petroleum resin (A) ..... The five sections (C5 system petroleum fraction (isoprene) / C5 system petroleum fraction (piperylene) / isopropenyl toluene = a monomer weight ratio (1.5/1.5/97), softening temperature: 125 degree C)

[0059] After it kneaded the above-mentioned mixture by the extruder and the grinder of a surface grinding method ground, a fine grain and coarse grain were classified with the wind-force type classifier, and the volume mean-particle-diameter  $d_{50}=8.0$ micrometer Magenta toner particle was obtained.

[0060] To the toner 100 obtained section, the negative triboelectric charging silica 1.0 section of 40nm of mean diameters and the negative triboelectric charging titania 0.5 section of 15nm of mean diameters were added, and it considered as the externally adding toner. The measurement result of the BET surface area measured with shape factor SF-1 by the image analyzer (roux ZEKKUSU 5000, Japanese regulator company make) of these toners (the number of samplings: 100 pieces) and SF-2, and specific surface area and a pore distribution measuring device (coal tar SA3100 mold, coal tar company make) is shown in a table 1. Next, to said externally adding toner 6 section, the carrier 100 section which covered the styrene methacrylate copolymer to the ferrite with a particle diameter of 50 micrometers was added, it mixed, and the developer was manufactured.

[0061] 5cm long and a 4cm wide solid non-established toner image were formed in the transfer paper of A4 using the developer <assessment of offset [-proof] nature> Obtained with the commercial electrophotography copying machine (A-Color630, Fuji Xerox make). The toner image was formed so that the amount of toners might serve as 0.6 - 0.8 mg/cm<sup>2</sup> at this time. Next, the temperature of a fixation roll could be set up freely, and supply of the oil for mold release to a fixation roll was stopped using what converted said A-Color630 so that a monitor could be carried out, and it tested on parenchyma in the condition that the oil for mold release does not exist in the front face of a fixation roll. That is, the skin temperature of a fixation roll was changed gradually and the non-established toner image on said transfer paper was established in each skin temperature. Under the present circumstances, it observed visually whether the toner dirt from a fixation roll would arise into the margin part of paper, and offset-proof nature was evaluated by making into a non-offsetting temperature field the temperature field which dirt does not produce. This result is shown in a table 1.

[0062] <assessment of preservation stability> -- said obtained toner 20g was put into the bottle made

from polyethylene with a volume of 150 cc, and was kept with the 47-degree C thermostat for 24 hours. After cooling radiationally to a room temperature (25 degrees C), that from which O and welding pose a problem as a matter of fact made x that in which a toner is observed visually and welding does not generate the welding condition between the ejection from a bottle, and a toner particle for it at all, and evaluated it. This result is shown in a table 1.

[0063] (Example 2) In the example 1, the outside which replaced copolymerization petroleum resin (A) with copolymerization petroleum resin (B) and (C5 system petroleum fraction (isoprene) / C5 system petroleum fraction (piperylene) / 98% isopropenyl toluene = monomer weight ratio (1.5/1.5/97) of purity and softening temperature: 125 degree C) was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}$ =8.0micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0064] (Example 3) In the example 1, the outside which replaced Wax A with Wax B (purification granular carnauba wax, \*\*\*\* chemistry company make, endoergic initiation temperature: about 50 degrees C, o'clock of 120-degree-C melt viscosity: 40 centipoise) was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}$ =7.6micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0065] (Example 4) In the example 1, the outside which replaced Wax A with Wax C (120 degree-C [ behenic acid ethylene glycol, endoergic initiation temperature: 60 degree C and ] o'clock of melt viscosity: 110 centipoises) was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}$ =6.5micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0066] (Example 5) In the example 1, the outside which replaced Wax A with wax D (120 degree-C [ oxalic acid hepta-thoria contour Norian, endoergic initiation temperature: 56 degree C, and ] o'clock of melt viscosity: 150 centipoises) was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}$ =7.3micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0067]

(Example 6)

a line -- polyester ..... The 88 sections (4,600 terephthalic acid the line obtained from /bisphenol A and an ethylene oxide addition product / bisphenol A and a propylene oxide addition product / cyclohexane dimethanol polyester: Tg= 70 degrees C, Mn= Mw= 38,000 acid number = 11 and water acid-number = 23)

Cyanogen pigment ..... The three sections (beta mold phthalocyanine: C.I. pigment blue 15:3) Wax A ..... The five sections (120 degree-C [ said behenic acid stearyl, endoergic

initiation temperature: 47 degree C, and ] o'clock of melt viscosity: 50 centipoises)

Copolymerization petroleum resin (A) ..... The four sections (said C5 system petroleum fraction (isoprene) / C5 system petroleum fraction (piperylene) / isopropenyl toluene = a monomer weight ratio (1.5/1.5/97), softening temperature: 125 degree C)

[0068] After carrying out preliminary mixing of the above-mentioned mixture, it kneaded by EKUSUTORYUDA and the jet mill ground. It classified with the wind-force type classifier, and the volume mean-particle-diameter  $d_{50}$ =7.2micrometer cyanogen toner particle was obtained. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0069] (Example 7)

To an autoclave with an equipped with [composition of isopropenyl toluene indene copolymer (1)] impeller net volume of 1270ml, isopropenyl toluene and an indene by the mole ratio 50:50 So that the sum total amount of supply of isopropenyl toluene and an indene may become in h and 1.0l. / The boron

truffe RORAIDO phenolate complex (1.6 times many phenol [ as this ] equivalent) diluted with isopropenyl toluene, an indene, the toluene that carried out dehydration purification, and the toluene which carried out dehydration purification 10 times was supplied continuously, and carried out the polymerization reaction with the reaction temperature of 5 degrees C. After transporting a reaction mixture to the 2nd step of autoclave succeedingly and continuing a polymerization reaction at 5 degrees C, the reaction mixture was discharged continuously in the place where the sum total residence time in the inside of the 2nd step of autoclave became the 1st step in 2 hours, and the polymerization reaction was terminated in the place used as 3 times of the residence time. The 1-N NaOH water solution was added to the reaction mixture after polymerization termination, and the polymerization reaction was stopped. After a lot of water washed the obtained reaction mixture 5 times, reduced pressure distilling off of a solvent and the unreacted monomer was carried out by the evaporator, and the isopropenyl toluene indene copolymer (1) was obtained. At this time, it was softening temperature  $T_m=145$  degree C, number-average-molecular-weight  $M_n=1190$ , and weight-average-molecular-weight  $M_w=2040$ .

[0070] In the example 6, the outside which replaced copolymerization petroleum resin (A) with the isopropenyl toluene indene copolymer (1) was produced like the example 6, and obtained the volume mean-particle-diameter  $d_{50}=6.8$ micrometer cyanogen toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0071] (Example 1 of a comparison) In the example 1, hot blast processing was further performed after classification, and the Magenta toner particle near a volume mean-particle-diameter  $d_{50}=8.5$ micrometer globular form was obtained. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0072] (Example 2 of a comparison) In the example 1, the outside which repeated the process in which classified a fine grain and coarse grain with a wind-force type classifier, and the particle of the medium size was obtained, 3 times after it kneaded mixture by the extruder and the grinder of a surface grinding method ground was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}=8.0$ micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0073] (Example 3 of a comparison) In the example 1, the outside which replaced Wax A with Wax E (120 degree-C [ KONORU 30F, the New Japan Chemical Co., Ltd. make, endoergic initiation temperature:37 degree C, and ] o'clock of melt viscosity: ten centipoises) was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}=6.4$ micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0074] (Example 4 of a comparison) In the example 1, the outside which replaced Wax A with Wax F (120 degree-C [ polypropylene, weight-average-molecular-weight:8300, endoergic initiation temperature:60 degree C and ] o'clock of melt viscosity: don't fuse) was produced like the example 1, and obtained the volume mean-particle-diameter  $d_{50}=6.4$ micrometer Magenta toner particle. To the obtained toner particle, a shape factor and BET surface area were measured like the example 1, and assessment of offset-proof nature and preservation stability was performed.

[0075]

[A table 1]

|       | WAX 假熱<br>開始温度<br>(℃) | 120℃の<br>熔融粘度(ポア<br>ズ) | SF-1 | SF-2 | BET表<br>面積 | 保存<br>性 | 非オフセット温度<br>領域 (℃) |
|-------|-----------------------|------------------------|------|------|------------|---------|--------------------|
| 実施例 1 | 47                    | 50                     | 148  | 123  | 2.1        | ○       | 120~190            |
| 実施例 2 | 47                    | 50                     | 145  | 115  | 2.0        | ○       | 120~180            |
| 実施例 3 | 50                    | 40                     | 150  | 120  | 2.4        | ○       | 120~190            |
| 実施例 4 | 60                    | 110                    | 153  | 130  | 2.6        | ○       | 120~200            |
| 実施例 5 | 58                    | 150                    | 140  | 120  | 1.9        | ○       | 130~180            |
| 実施例 6 | 47                    | 50                     | 146  | 126  | 2.2        | ○       | 130~190            |
| 実施例 7 | 47                    | 50                     | 140  | 125  | 2.2        | ○       | 130~190            |
| 比較例 1 | 47                    | 50                     | 115  | 106  | 1.3        | ○       | 130~150            |
| 比較例 2 | 47                    | 50                     | 125  | 115  | 1.4        | ○       | 130~160            |
| 比較例 3 | 37                    | 10                     | 143  | 123  | 2.0        | ×       | 110~170            |
| 比較例 4 | 60                    | 溶解せず                   | 150  | 128  | 2.3        | ○       | 160~190            |

[0076] From the result of a table 1, when the toner for electrophotography of this invention of examples 1-7 is used, the non-offsetting temperature field is crossed to the large area from low temperature to high temperature, and is understood that offset-proof nature is good. Moreover, preservation stability was also satisfactory. On the other hand, although preservation stability was satisfactory when the toner for electrophotography of the examples 1, 2, and 4 of a comparison was used, the non-offsetting temperature field was narrow and offset-proof nature was bad. Moreover, preservation stability was bad, although the non-offsetting temperature field had shifted to the low temperature side and it was crossing broadly, when the toner for electrophotography of the example 3 of a comparison was used.

[0077]

[Effect of the Invention] According to this invention, it excels in fine-particles properties, such as preservation stability, and the good toner for electrophotography of offset-proof nature, a binary system developer, and the image formation approach using it can be offered.

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[Translation done.]